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[1]

Role of Gas Chromatographic Retention Index in Compound Identification System of Mass Spectra

Keiko Masumoto and Takeshi Yamamoto

Abstract

Pre-search using gas chromatographic retention indices reinforce computer aided compound identification by the mass spectral retrieval method. This advantage of gas chromatographic information is more significant in the GC/MS analysis of environmental samples of complex chemical constituents.

We developed a library search system for mass spectra which was limited to the environmentally interesting chemicals. The system comprises pre-search involving gas chromatographic retention windows and main search on the basis of the similarity index.

The application of this search system on the GC/MS analysis of sea water and sediment sample extracts revealed the improved reliability and reduced retrieval period.

Key words: Gas chromatography, Mass spectrometry, Computer retrieval system, Compound identification, Sea water, Sediment

Introduction

In the analysis of chemical substances in the environment, bulk analysis of multi-component chemical substances contained in samples and the search for substances whose presence is unknown are often done, for which, as the analytical means, gas chromatographic mass spectrometry (GC/MS) is extremely effective. Taking the opportunity provided by the introduction of the U.S. EPA/NIH/MSDB mass spectral data base, the development of a GC/MS/COM automated search system was carried out,[1-3] and also developing a three-dimensional mass chromatography (TDMC) program that effectively removes the mixed peaks attributable to insufficient GC

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separation,[4,5] basic experiments on them and their application to environmental samples have been attempted. However, as far as analyzing actual environmental samples is concerned, these systems have not necessarily fulfilled their functions satisfactorily. This is because of problems with the insufficiency of component separation in GC and the lowness of reliability of the mass spectra stored in the data base.

Furthermore, even if mass spectra of high quality were to be obtained, there are cases where the target substance cannot be correctly detected by a search using mass spectral data alone. Even if the mass spectra are alike, numerous examples can be seen where the GC retention time differs. In such cases it would be effective to utilize the GC separation data, but at the present time a mass spectral data base with a GC retention index is virtually non-existent.

Accordingly, in order to cope with such problem points in environmental analysis, a data base of high quality containing GC data was formulated, and a GC/MS data search system suited to environmental analysis was developed and applied to actual environmental samples, so a report is hereby made.

I. Construction of search data base

1. GC retention index

Among the mass spectral search methods are the Similarity Index (SI) method[6] and Probability Based Matching (PBM) method[7] and such, and developing these programs, they have been applied to actual environmental samples as well.[7] However, in the case of substances whose mass spectra are alike such as fatty acid methyl esters as in Fig. 1, from the index of matching after retrieval by the SI method or PBM method, it is difficult to judge which substance a measured substance is.

The GC retention index obtainable when separating mixed components into single components by gas chromatography (GC) has been used from before as a means of identification by GC alone such as by changing the separation column and

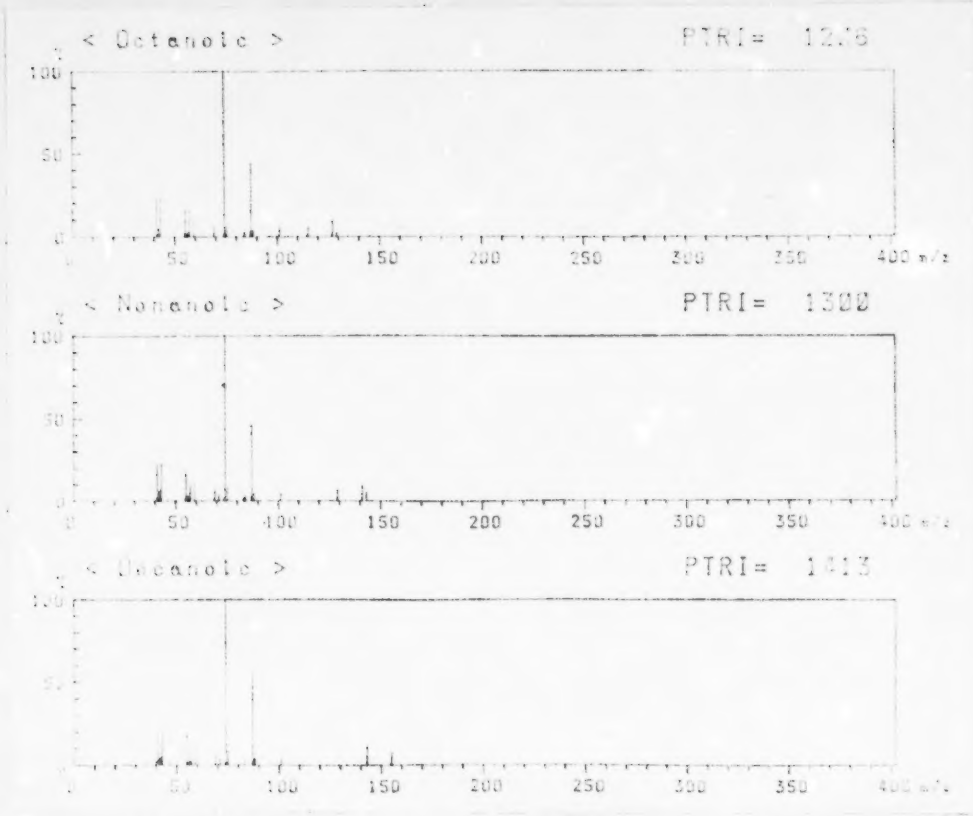

Fig. 1. Mass spectra of fatty acid methyl esters

Upper: Octanoic acid methyl ester
Middle: Nonanoic acid methyl ester
Lower: Decanoic acid methyl ester

making it match. By adding this retention index into the data base as well and utilizing it as part of the search parameters, an improvement in search efficiency can be anticipated.

As the retention index, the gas chromatographic retention index under rising temperature conditions (Programmed Temperature Retention Index = PTRI) shown in Equation 1 is used. For the liquid phase of the column, however, this [2]

Equation 1. PTRI calculation formula

$$PTRI = 100 \cdot (Z + (T_x - T_z)/(T_{z+1} - T_z))$$

$T_z < T_x < T_{z+1}$

Z: Carbon no. of n-alkane C_z

T_z, T_{z+1}: Retention time of n-alkane C_z, C_{z+1}

T_x: Retention time of unknown material

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must be determined beforehand. This search system being a system for separating and identifying multi-component chemical substances in environmental samples, it differs from a mass spectral search for single components, and the means of separation and control of accuracy are considered to be part of the data analysis as well. By selecting the optimum column liquid phase in that sense and storing its retention index only and utilizing it as a search parameter, the complication of liquid phase selection at search time can also be avoided.

For GC accuracy control, appropriate standard substances are measured and a check of the variation in PTRI is done. Fig. 2 is a chromatogram measured by adding naphthalene, anthrathene and fluoranthene to n-alkane of carbon number 12-24.

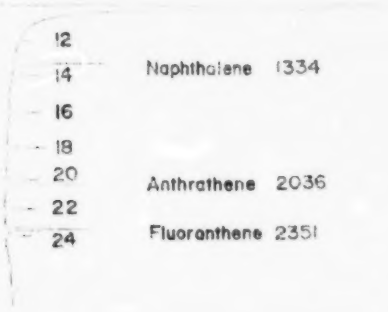

Fig. 2. Chromatogram of naphthalene, anthrathene, fluoranthene, n-alkane (carbon number 12-24)

Based on Equation 1, the PTRI for naphthalene turns out to be 1334, for anthrathene 2036 and for fluoranthene 2351. When measuring actual environmental samples, stable isotopes of naphthalene and such are added to the sample to provide a yardstick for variation. [3]

2. Mass spectral data

Because the mass spectra to be stored must be of high quality, standardization of the measurement conditions when measuring the standard substances is required. However, in that the conditions whereby mass spectra which satisfy a set standard are measurable would vary by apparatus, it is indispensable that

accuracy control be undertaken beforehand such as by measuring the standard substances to be used as the yardstick with that apparatus and calibrating it.[8,9)]

Using bis (pentafluoro phenyl) phenyl phosphine (BPFPP) for the standard substance and determining R (= sum of the strength of principal characteristic peaks/sum of the strength of impure peaks) for the evaluation of accuracy, the measurement conditions are determined. Fig. 3 is the variation in R when measured by varying the injected quantity of BPFPP. The measurement conditions are shown below.

Table 1

Analytical apparatus	Nippon Electronics DX-303
Data processing apparatus	Ditto DA-5000
Column	3 mmφ x 2 m glass column
	Silicone OV-17 2% on Chromosorb W (AW-DCMS)
	80/100 mesh
Carrier gas	He 30 mL/min
Injection temperature	200°C
Column temperature	200°C
Ionization method	EI
Separator temperature	210°C
Ion source temperature	210°C
Ionization energy	70 eV
Ionization current	300 μA
Acceleration voltage	3 kV
Ionic multi - voltage	1.2 kV
Scan range	m/z 50-500
Scan time	1 sec

It is thought desirable to measure the standard substances to be stored in the data base at conditions of $R \geq 5$. Furthermore, it is essential that such accuracy controls be always undertaken.

3. Utilization of structural characteristic ion data of chemical substances

Among the ions which exhibit structural characteristics are molecular ions,

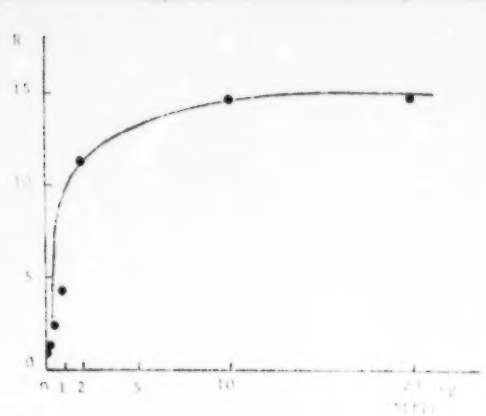

Fig. 3. Relationship between injected quantity of bis (pentafluoro phenyl) phenyl phosphine and mass spectral quality R

base peaks, neutral-deficient ions, other characteristic fragment ions and such, which, even though low in relative strength, are ions that always emerge. If the ions high in strength match, with the SI method a high evaluation will be provided regardless of the presence or absence of structure-specific ions, so that should a match of structural characteristics ions be confirmed, the reliability will increase. For that reason there is a need to store these ions in the data base. In addition to the base peaks and molecular ions, the neutral-deficient ions and characteristic fragment ions are stored by selecting three low mass peaks and three high mass peaks.

II. Outline of search program

This program is one that was written aimed at system development suited to the objective of environmental analysis, so that in order to enable processing and study within the laboratory, a personal utility has been aimed for. For that reason the reference data capacity has been made small, and consideration was given to shortening the time required for search as well.

For the development, an NEC-PC 9801 (language: BASIC) and an IBM Series 1 (language: FORTRAN) were used.

1. Compilation of data file

The data file consists of a PTRI Table, mass spectral file and structural characteristic file, and in the structural characteristic file in the mass spectral file the data on each stored substance are arranged in order of magnitude of PTRI. In the PTRI Table, only the PTRI has been input arranged in this order.

In the mass spectral file, spectral data up to a maximum of 31 peaks selected according to the Biemann method[6] have been stored, trying not to exceed a data length of 128 bytes per substance.

In the structural characteristic file, in addition to the structural characteristic ions aforementioned, chemical substance names, molecular equations and CAS No. have been stored, and using a data length of 128 bytes per substance, in cases where the name is especially long it was made expandable up to 256 bytes.

The number of substances stored at present is 480 but counting those in the process of renewal as well it comes to approximately 600 substances, including [4] those measured by GC/MS at the regional pollution laboratories.

2. Search algorithm

A flow chart of this program is shown in Fig. 4. First of all, the selection of the device to input the measured sample mass spectra and the device to output the search results as well as the parameters of the search conditions and such are established. Next, the PTRI and mass spectra are input, by keyboard in the case of keyboard input or by file in the case of file input of a disk and such in which the measured sample data have been input beforehand.

Next, from the PTRI that has been input, making reference to the PTRI Table, substances close to that PTRI in the reference data are selected out. Then reading the data on those substances from the mass spectral file, a calculation of the SI value is done based on the SI method. The SI, as shown in Equation 2, has a numerator which is a weighted average of the strength ratios of those whose peaks have matched and a denominator which is 1 plus the ratio of the unmatched

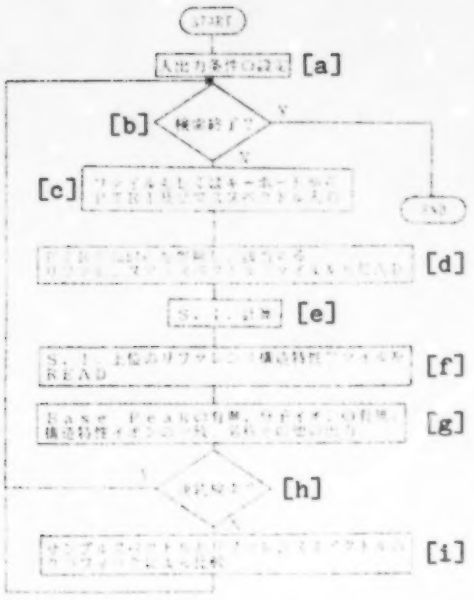

Fig. 4. Flow chart of PTRI-fed mass spectral search program

[a] Establishment of input/output conditions
[b] Search completed?
[c] Input PTRI and mass spectra from file or keyboard
[d] Referring to PTRI Table, read applicable reference mass spectral file
[e] S.I. calculation
[f] Read reference structural characteristic file above S.I.
[g] Presence or absence of base peak, presence or absence of molecular ions, matching of structural characteristic ions, names and other things output
[h] Continuous search?
[i] Comparison by graphics of sample spectra and reference spectra

ion volume to the total ion volume, and in this system, looking at it from the sample spectra, it is calculated by the reverse search method which evaluates the match or non-match of the respectively retrieved reference spectra. In the case where the similarity is highest, SI = 1 obtains.

Next, selecting those substances with a SI higher than the SI threshold set as part of the search conditions and reading the data on these substances

Equation 2. SI calculation formula

$$SI = \frac{\sum W_i (I_i^U / I_i^R) / \sum W_i}{1 + \frac{\sum I_k^U + \sum I_k^R}{\sum I_i^U + \sum I_i^R}}$$

from the structural characteristic file, the matching of the base peak, the presence or absence of molecular ions and the matching of structural characteristic ions are checked, and these data are output onto the specified output device in order of high SI.

In the case of continuous search, returning to the sample data input, the search is repeated.

Also in the case where it is desired to throw in a detailed study, it would be possible to display on the screen the reference spectra retrieved and the sample spectra input and compare the unmatched peaks and such.

3. Method of use

For inputting the measured PTRI and mass spectra, a program editor of the system is used, and a special program for input purposes is not required. Additions, deletions and such revisions can also be simply handled similar to normal program writing and revision, and can be saved on a floppy disk. Fig. 5 is an example of a sample data input where a NEC-PC 9801 was used. Fig. 6 shows the results obtained when the sample data in Fig. 5 were searched. As the search conditions, the PTRI window was set at ±25, and the SI calculation was only to be

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Fig. 5. Example of sample data input

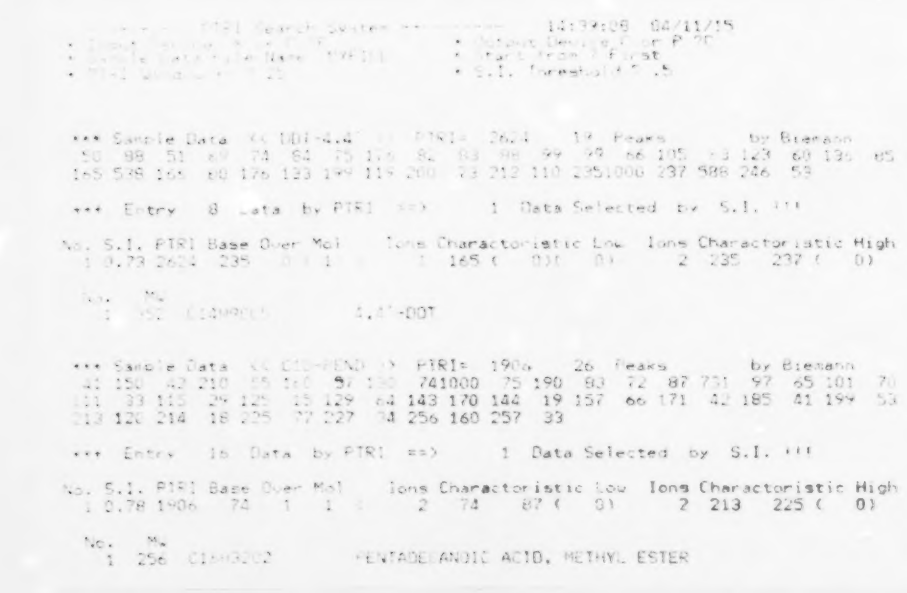
On lines 100 and 170 as numbered at left the sample name (8 characters), PTRI, number of peaks are input, below which the m/z and relative strength (strongest 1000) are input.

done for the spectral data of substances falling within that range. Also by setting the SI threshold at 0.5, the output of data for ones below 0.5 would be precluded.

The search system reads in the spectra from the input file giving these search conditions, processes by the Biemann method and produces an output. Next the number of substances falling within range in PTRI (in Fig. 6, 8 substances in the upper sample and 16 substances in the lower sample) is indicated. [6]

(See the explanation of search results in Table 2)

Determining the similarity between the substances retrieved in this way and the samples, that is, the SI value, those substances above the SI threshold are selected and ranked. After checking the structural characteristic ions and such, their data is output. The upper sample in Fig. 6 turned out to be 4,4'-DDT, and the lower sample pentadecanoic acid methyl ester. The sample data input being 4,4'-DDT and pentadecanoic acid methyl ester listed in the literature, it can be seen that a correct retrieval was made. [5]



```
                    PTRI Search System ----------        14:39:08  04/11/15
 * Input Device = C:F1.DAT          * Output Device = or P.RT
 * Sample Data File Name = MYFILE   * Start from 1 First
 * PTRI Window = +/- 25             * S.I. Threshold = .5

*** Sample Data  <<  DDT-4,4'  >>  PTRI=  2623    10 Peaks        by Biemann
 50  98  51  69  74  64  75 170  86  83  98  99  99  66 105  23 123  60 136  65
145 538 164  60 176 123 199 119 200  73 212 110 2351000 237 508 246  59

*** Entry  8  Data by PTRI  ***      1  Data Selected by  S.I. ***

No. S.I. PTRI Base Over Mol    Ions Characteristic Low   Ions Characteristic High
  1 0.73 2624  235    0    1    1  165 (   0)   0)      2  235   237 (   0)

 No.   Mw
   1   352  C14H9Cl5          4,4'-DDT

*** Sample Data  <<  C16-MEND  >>  PTRI=  1906    26 Peaks        by Biemann
 41 150  42 210  55 160  57 130  741000  75 190  83  72  87 731  97  65 101  70
111  33 115  24 125  15 129  64 143 170 144  19 157  66 171  42 185  41 199  53
213 120 214  18 225  77 227  74 256 160 257  33

*** Entry  16  Data by PTRI  ***      1  Data Selected by  S.I. ***

No. S.I. PTRI Base Over Mol    Ions Characteristic Low   Ions Characteristic High
  1 0.78 1906   74    1    1    2   74    87 (   0)      2  213   225 (   0)

 No.   Mw
   1   256  C16H32O2          PENTADECANOIC ACID, METHYL ESTER
```

Fig. 6. Search results using sample data in Fig. 5
Searched using a PTRI search range of ±25, S.I. threshold of 0.5.
For explanation of results, see Table 2.

Table 2. Explanation of search results

*** Sample Data ... by Biemann

Mass spectra selected from the sample data using the Biemann method.

+++ Entry 8 Data by PTRI

The number of data within the range of PTRI ± 25 in the sample data was eight.

==> 1 Data Selected by S.I. !!!

The number of data whose value of S.I. was 0.5 or higher was one.

No.

Ranking in order of high S.I.

S.I. PTRI

S.I. and PTRI of the reference data retrieved.

Base

Mass number of the base peak of the reference data. Where enclosed in parenthesis, there is no base peak of the sample data in the reference data.

Over

Number of peaks present in the sample data with a mass number higher than the maximum mass number of the reference data.

Mol

Where molecular ions are present in the reference data, 1; where not present, 0. Where enclosed in parenthesis, there are no molecular ions of the reference data present in the sample data.

> or <

When a peak of a mass number higher than the molecular weight of the reference data is

present in the sample data <

not present in the sample data >

Ions Characteristic Low & High

Number of structural characteristic ions (low, high) and mass number. Those enclosed in parenthesis indicate no presence in the sample data.

No. MW

Ranking by S.I., molecular weight, followed by molecular formula and name.

III. Application to environmental samples

The PTRI and mass spectra of the chemical substances in environmental samples, by virtue of the GC separation and refinement being insufficient or the peak of the target substance being hidden because of high background and turning into a mixed spectrum, exert a great effect on the search efficiency. In order to examine to what extent this search system is adaptable to such problem points and what kind of improvements including measurements should be incorporated, as environmental samples water samples and sediment samples from outside Osaka Harbour and the rivers within Osaka City were used, and adding 41 types of chemical substances shown in Table 3, an evaluation of the recovery rate and search parameters was done.

Table 3. Table of standard substances

1	o-chlorotoluene	22	Dimethyl phthalate
2	p-dichlorobenzene	23	α-naphthylamine
3	o-dichlorobenzene	24	Pentachlorobenzene
4	2,4-dichlorotoluene	25	3,4-dinitrotoluene
5	1,2,4-trichlorobenzene	26	4-chloro-2-nitroaniline
6	m-dibromobenzene	27	1-nitronaphthalene
7	m-nitrotoluene	28	Diethyl phthalate
8	p-diisopropyl benzene	29	4,4'-dimethylbiphenyl
9	2,3-xylidine	30	Diphenylamine
10	p-chlorophenol	31	p-tert-octyl phenol
11	p-chloronitrobenzene	32	Tributyl phosphate
12	o-chloro-2-methylaniline	33	Diisopropyl naphthalene
13	α-methylnaphthalene	34	γ-BHC
14	2,4-dichloroaniline	35	Pentachloronitrobenzene
15	2,4-dichloronitrobenzene	36	Anthrathene
16	2,4,5-trichlorophenol	37	Diethyl biphenyl
17	1,2,3,4-tetrachlorobenzene	38	Triethyl biphenyl
18	p-nitroanisole	39	Dibutyl phthalate
19	Biphenyl	40	p-terphenyl
20	Diphenyl ether	41	Triphenyl phosphate
21	m-dinitrobenzene		

1. Experimental method

The 41 standard substances were added so as to constitute 0.5 μg/L in the water samples and 10 μg/kg in the sediment samples, processing them in accordance with the "Manual on search for chemical substances in the environment using GC/MS (Draft)" compiled by the Health Research Laboratory of the Environmental Agency. The GC/MS analysis conditions are shown below. [7]

Analytical apparatus	Nippon Electronics DX-303
Data processing apparatus	Ditto DA-5000
Column	(PAC denotes a packed column and CAP denotes a capillary column.)
PAC	3 mmφ x 2 m glass column Silicone OV-17 2% on Chromosorb W (AW-DCMS) 80/100 mesh
CAP	0.32 mmφ x 25 m, membrane thickness 0.52 μm, chemical bonding-type fused quartz capillary column OV-1
Carrier gas	
PAC	He 30 mL/min
CAP	He 2.5 mL/min
Injection temperature	250°C
Column temperature	80-250°C (temperature rise 4°C/min)
Injection method	
PAC	On-column method
CAP	Solventless method (Moving needle method)
Ionization method	EI
Separator temperature	250°C
Ion source temperature	250°C
Ionization energy	70 eV
Ionization current	300 μA
Acceleration voltage	3 kV
Ionic multi - voltage	1.2 kV
Scan range	m/z 50-500
Scan time	
PAC	1 sec
CAP	0.5 sec

2. Packed column and capillary column

Because high-quality mass spectra of environmental samples cannot be obtained due to mixed components and background peaks which must be removed, they exert a big effect on search efficiency.

Accordingly, a capillary column which separates mixed components extremely efficiently was used, and comparing it with the erstwhile packed column, the effect on search efficiency was examined.

First of all the PTRI of the 41 substances was determined and the interchangeability of PTRI between the two was examined. As shown in Fig. 7, a high correlation was seen between the two, with the regression equation turning out as

$$Y = 1.23x - 541 \text{ (correlation coefficient 0.984).}$$

At the time of search, however, because the PTRI values based on a packed column are stored in the reference data base, the PTRI values from the capillary column were converted to PTRI values for a packed column to do the search.

The PTRI values based on a packed column have been shown in Table 4. However, because diisopropyl naphthalene, diethyl biphenyl and triethyl biphenyl were mixtures of position isomers, representative values were selected for the PTRI value.

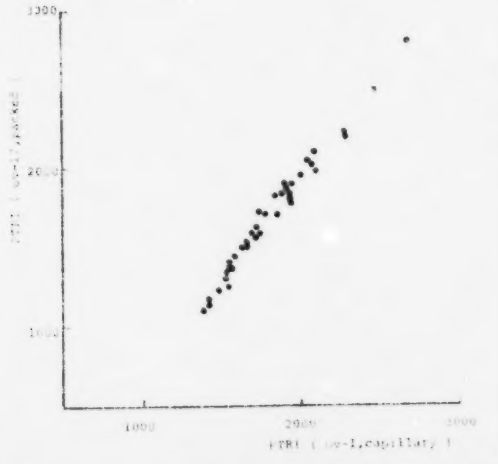


Fig. 7. Correlation between PTRI of packed column (OV-17) and capillary column (OV-1)

3. Additive recovery experiment

The fractionation process was done according to the manual (draft). The fraction no. in Table 4 is the no. in the neutral fraction. p-chlorophenol and 2,4,5-trichlorophenol were extracted from the acid fraction, but the rest were extracted from the neutral fraction.

In Table 4 has been shown the recovery rate of the added standard substances in the water samples and sediment samples by capillary column. The reason why the recovery rate of substances low in PTRI is low is thought to be because the solventless method was used as the injection method due to which the substances low in boiling point volatilized together with the solvent. Where 100% is exceeded is because that substance was already present in the sample.

The total ion chromatogram (TIC) of each sample has been shown in Fig. 8-1 to Fig. 8-7. *N, *A, *F in the figures denote the peaks for the internal standard substances naphthalene-d_8, anthrathene-d_{10}, fluoranthene-d_{10}, respectively. The heights of the peaks in each figure have been normalized to the strongest peak in the respective samples.

The horizontal axis is time, with the lower scale being the scan number and the upper scale being the retention time in minutes.

In the capillary (CAP) TIC almost all the standard substances are separated and sharp peaks are formed, but in the packed (PAC) TIC the peaks are broad and overlapping.

The peak positions of the 41 substances have been shown in Figs. 9-1-a, b, c, d (Fig. 8-2 split into four parts) and Figs. 9-2-a, b, c (Fig. 8-3 split into three parts). The numerals in the figures correspond to the standard substance number in Table 3. [10]

In the packed column case, because a number of peaks are overlapping as in Fig. 9-2-b, it is difficult to extract the target standard substance and

Table 4. PTRI and additive recovery rate (%) of standard substances [8]

表4 標準物質の PTRI と添加回収率 (%)

	[a] 物質名	[b] 水質	[c] 底質	[d] 分画 no.	PTRI
1	o-クロロトルエン [e]	—	—		1100
2	p-ジクロロベンゼン	22	262	1	1135
3	o-ジクロロベンゼン	21	38	1	1170
4	2,4-ジクロロトルエン	—	30	2	1231
5	1,2,4-トリクロロベンゼン	27	41	1	1310
6	m-ジブロモベンゼン	23	33	1	1355
7	m-ニトロトルエン	23	34	2	1403
8	p-ジイソプロピルベンゼン	14	27	1	1260
9	2,3-キシリジン	—	—		1390
10	p-クロロフェノール	23 a	—		1370
11	p-クロロニトロベンゼン	35	33	2	1435
12	o-クロロ-2-メチルアニリン	—	—		1498
13	α-メチルナフタレン	39	177	1, 2	1496
14	2,4-ジクロロアニリン	—	35	2	1540
15	2,4-ジクロロニトロベンゼン	44	53	2	1585
16	2,4,5-トリクロロフェノール	63 a	—		1520
17	1,2,3,4-テトラクロロベンゼン	42	44	1	1557
18	p-ニトロアニソール	37	81	2	1628
19	ビフェニール	42	115	2	1573
20	ジフェニルエーテル	36	111	2	1568
21	m-ジニトロベンゼン	43	57	1	1735
22	フタル酸ジメチル	56	25	2	1702
23	α-ナフチルアミン	—	—		1835
24	ペンタクロロベンゼン	45	47	1	1700
25	3,4-ジニトロトルエン	58	—		1835
26	4-クロロ-2-ニトロアニリン	53	—		1895
27	1-ニトロナフタレン	67	122	2	1875
28	フタル酸ジエチル	58	7	2	1835
29	4,4'-ジメチルビフェニール	49	115	2	1790
30	ジフェニルアミン	50	128	1, 2	1885
31	p-tert-ブチルフェノール	57	109	2	1760
32	リン酸トリブチル	65	22	1	1915
33	ヘキサクロロベンゼン	9	43	2	1853
34	γ-BHC	60	170	2	2050
35	ペンタクロロニトロベンゼン	52	—		2032
36	アントラセン	54	403	2	2100
37	ジエチルビフェニール	26	41	2	1974 +
38	トリエチルビフェニール	103	193	2	2129 +
39	フタル酸ジブチル	346	87	1	2211
40	p-ターフェニル	59	128	2	2489
41	リン酸トリフェニル	98	—		2800

内部標準 Internal standard

d_8-ナフタレン	d8-naphthalene	1345
d_{10}-アントラセン	d10-anthrathene	2030
d_{10}-フルオランテン	d10-fluoranthene	2340

注, aは酸性分画をしめす. Note: "a" denotes acid fraction.
+は代表値 "+" denotes representative value.

[a] Substance name
[b] Water sample
[c] Sediment sample
[d] Fraction no.
[e] [Substances listed identically to Table 3]

[9]

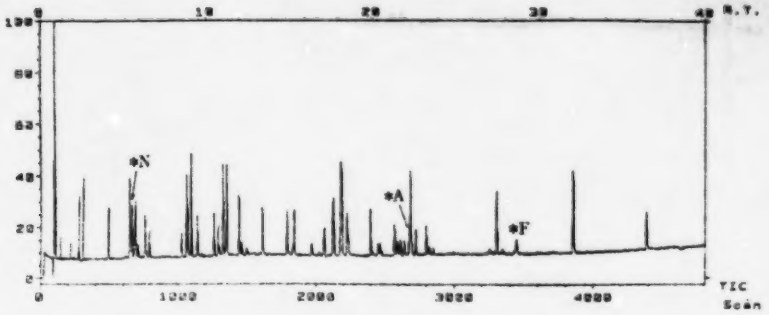


図8—1 全イオンクロマトグラム 標準物質 (CAP)

Fig. 8-1. Total ion chromatogram Standard substances (CAP)

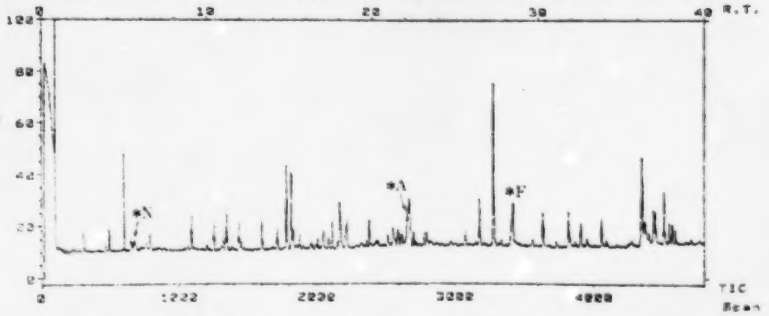


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図8—2 全イオンクロマトグラム 水質+標準 (CAP)

Fig. 8-2. Total ion chromatogram Water sample + standard substances (CAP)

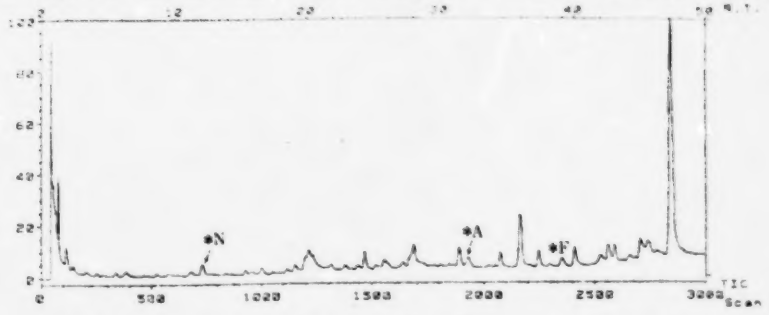

図8—3 全イオンクロマトグラム 水質+標準 (PAC)

Fig. 8-3. Total ion chromatogram Water sample + standard substances (PAC)

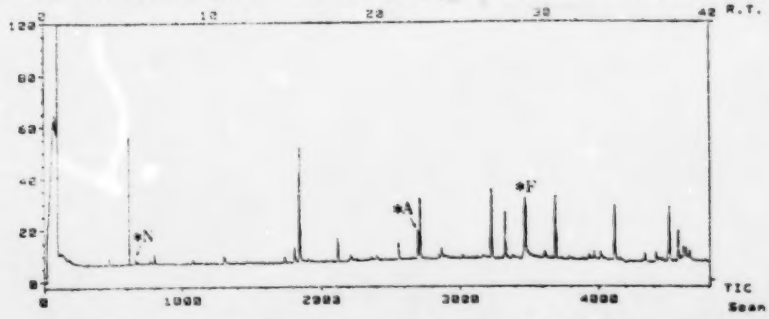

図8—4 全イオンクロマトグラム 水質+標準, 酸性分画 (CAP)

Fig. 8-4. Total ion chromatogram Water sample + standard substances; acid fraction (CAP)

[10]

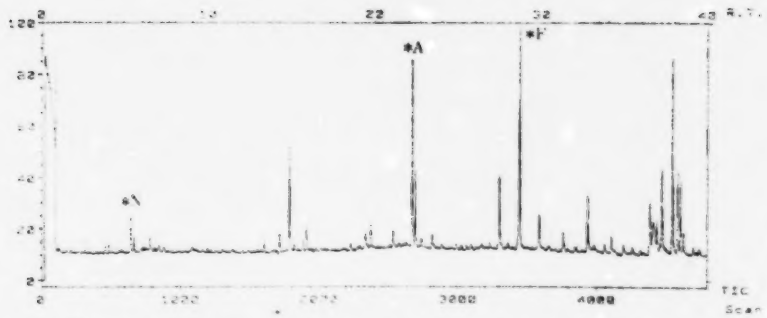

図8-5 ｸﾛﾏﾄｸﾞﾗﾑ 水質+標準, 塩基性分画 (CAP)

Fig. 8-5. Total ion chromatogram Water sample + standard substances; basic fraction (CAP)

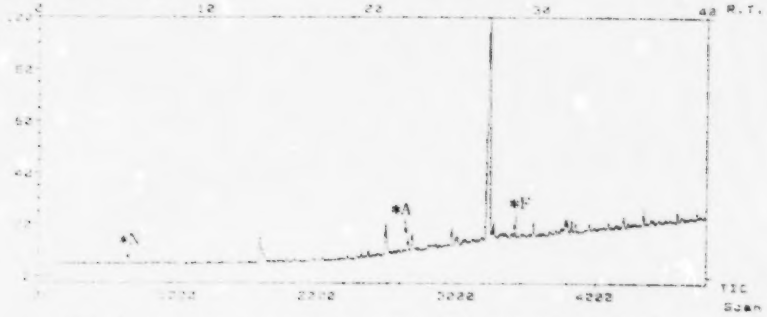

図8-6 ｸﾛﾏﾄｸﾞﾗﾑ 底質+標準, 中性分画-1 (CAP)

Fig. 8-6. Total ion chromatogram Sediment sample + std. substances; neutral fraction-1 (CAP)

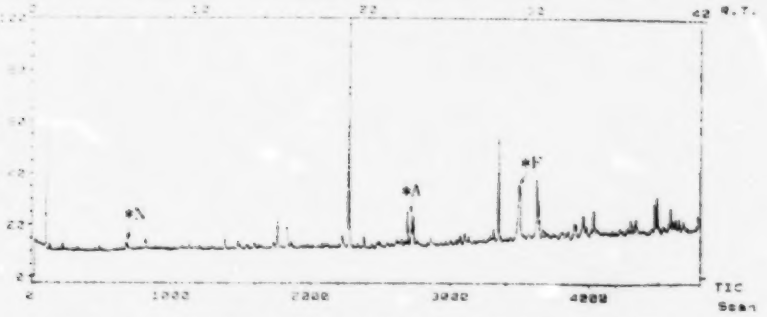

図8-7 ｸﾛﾏﾄｸﾞﾗﾑ 底質+標準, 中性分画-2 (CAP)

Fig. 8-7. Total ion chromatogram Sediment sample + std. substances; neutral fraction-2 (CAP)

carry out background processing. By contrast in the capillary column case, as shown in Figs. 9-1-b, c, separability is good, and the peaks not only of the added substances but of the unknown substances contained in the water sample as well have been separated.

The effect on the mass spectra of such insufficiency in peak separation in GC was examined. Fig. 10-1 is a mass chromatogram of diphenylamine (m/z 167, 168, 169), tributyl phosphate (m/z 99) and diisopropyl naphthalene (m/z 197).

[11]

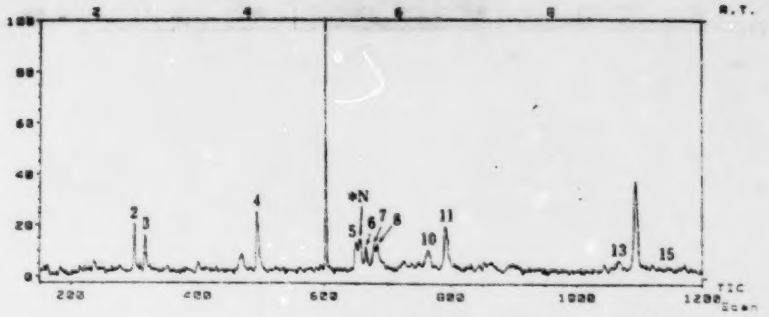

図9-1-a 全イオンクロマトグラム 水質+標準 (CAP) ¼ (~10分)

Fig. 9-1-a. Total ion chromatogram Water sample + std. substances (CAP) 1/4 (~10 min.)

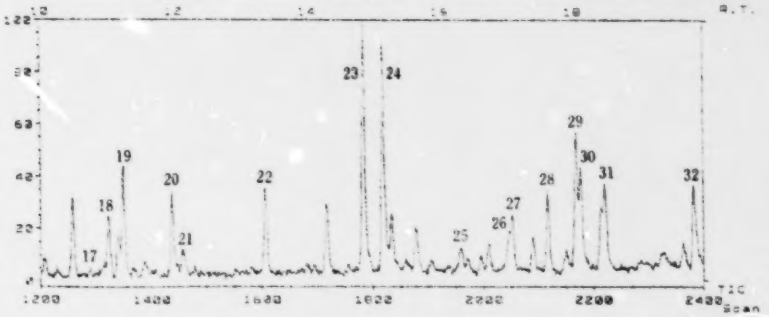

図9-1-b 全イオンクロマトグラム 水質+標準 (CAP) ¾ (10~20分)

Fig. 9-1-b. Total ion chromatogram Water sample + std. substances (CAP) 2/4 (10-20 min.)

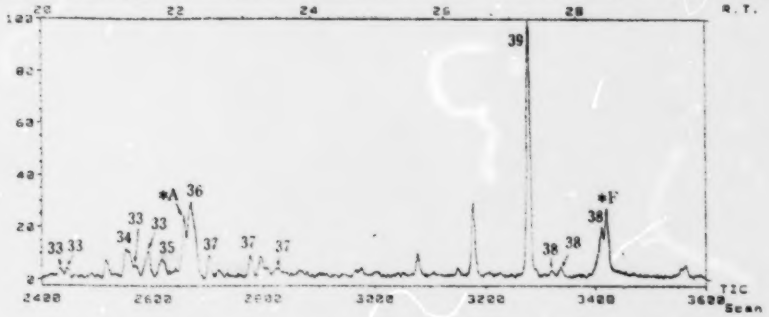

図9-1-c 全イオンクロマトグラム 水質+標準 (CAP) ¾ (20~30分)

Fig. 9-1-c. Total ion chromatogram Water sample + std. substances (CAP) 3/4 (20-30 min.)

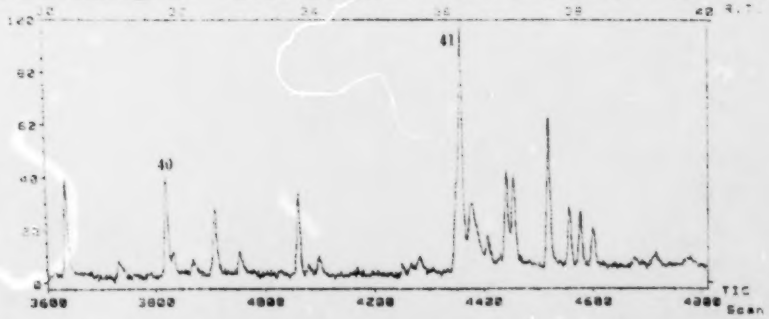

図9-1-d 全イオンクロマトグラム 水質+標準 (CAP) ¾ (30~40分)

Fig. 9-1-d. Total ion chromatogram Water sample + std. substances (CAP) 4/4 (30-40 min.)

[12]

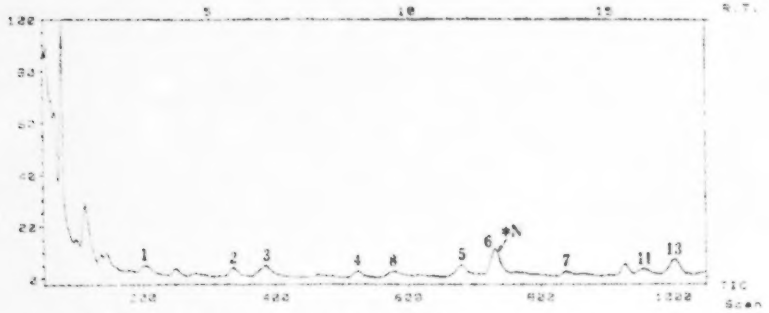

図9-2-a 全イオンクロマトグラム 水質+標準 (PAC) 1/3 (~17.5分)

Fig. 9-2-a. Total ion chromatogram Water sample + std. substances (PAC) 1/3 (~17.5 min.)

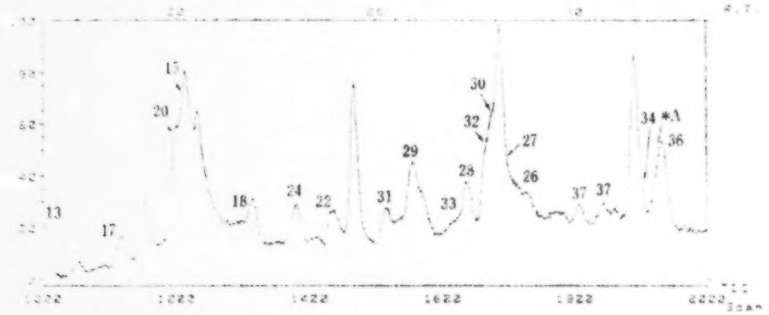

図9-2-b 全イオンクロマトグラム 水質+標準 (PAC) 2/3 (16.5~33.5分)

Fig. 9-2-b. Total ion chromatogram Water sample + std. substances (PAC) 2/3 (16.5-33.5 min.)

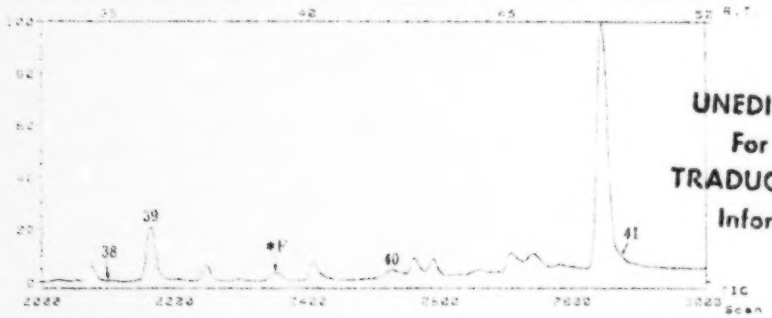

図9-2-c 全イオンクロマトグラム 水質+標準 (PAC) 3/3 (33.5~50分)

Fig. 9-2-c. Total ion chromatogram Water sample + std. substances (PAC) 3/3 (33.5-50 min.)

図10

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In the upper packed column figure, the peaks of these three substances are overlapping and it can be seen that background processing to compose the mass spectrum is difficult. On the other hand, in the lower capillary column figure, the three substances form peaks fairly well separated so they cannot be mixed up. Fig. 10-2 is a mass spectrum of diphenylamine (base peak m/z 169). The upper figure is based on a packed column and contains impure peaks such as at m/z 99, 197, 212. The lower figure is from a capillary column and a high-quality spectrum has been obtained.

In Figs. 11-1 and 11-2 have been shown the mass chromatograms and mass spectra of the added standard substance anthrathene and anthrathene-d_{10} added as an internal standard for calibration purposes. With the capillary column, even the peaks of the internal standard substance of the d-bodies are completely separated.

In Figs. 12-1 and 12-2 have been shown the mass chromatograms and mass spectra of diisopropyl naphthalene. Because this substance has position isomers mixed in, multiple peaks appear as in Fig. 12-1, but with the capillary column they are amply separated. However, as shown in Fig. 12-2, there is not much difference in quality with the mass spectrum based on a packed column. This is because with a packed column isomers are mixed in, and the mass number comprising their spectra being the same, the ion strength is higher than a single component, so even though they are mixtures the impure peaks are few.

In this way the mass spectra obtained from analysis using a capillary column are high in quality, and an improvement in search results can also be anticipated.

[13]

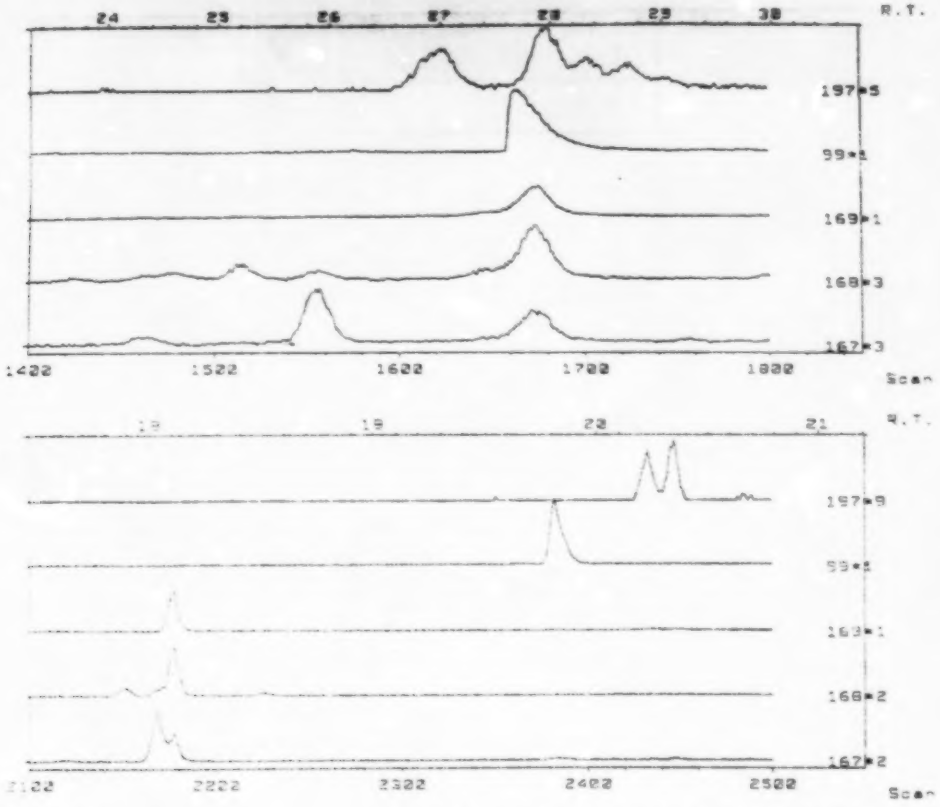

図10－1　ジフェニルアミン（m/z 167, 168, 169），リン酸トリブチル（m/z 99），ジイソプロピルナフタレン（m/z 197）のマスクロマトグラム（上はパックドカラム，下はキャピラリーカラムによるもの．右端の数字は質量数と表示倍率）

Fig. 10-1. Mass chromatograms of diphenylamine (m/z 167, 168, 169), tributyl phosphate (m/z 99) and diisopropyl naphthalene (m/z 197) (Upper figure is based on a packed column, lower on a capillary column. Numerals along right side are mass number and magnification.)

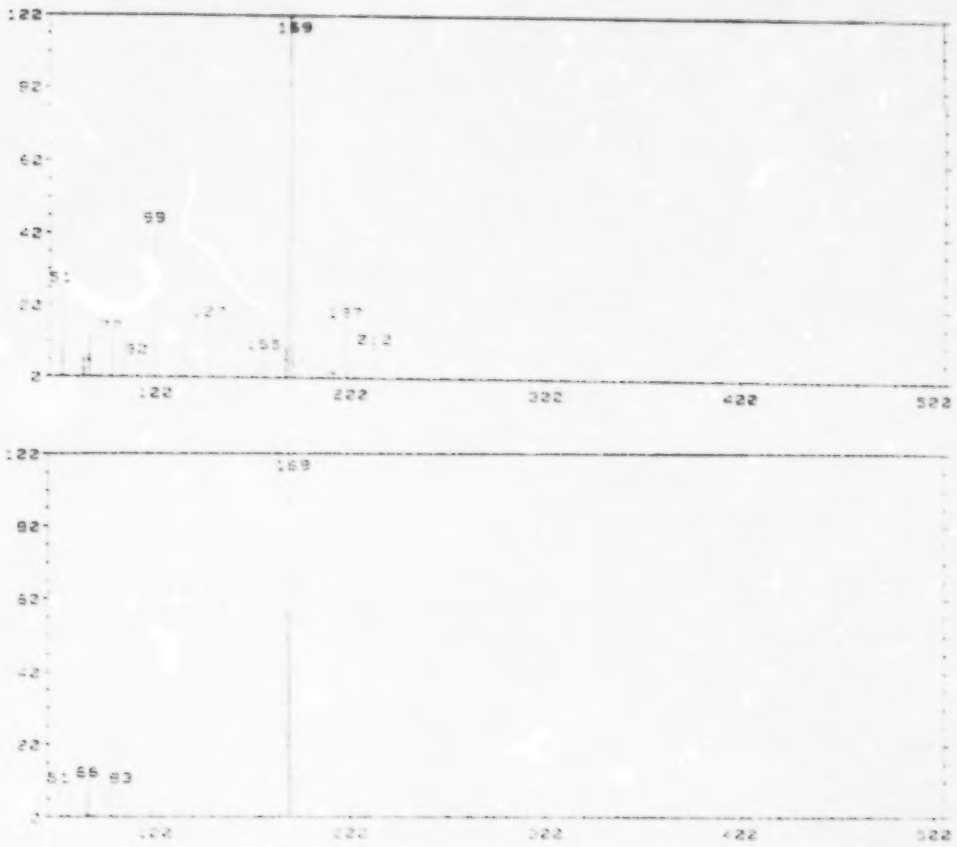

図10-2 ジフェニルアミンのマススペクトル
（上はパックドカラム，下はキャピラリーカラムによるもの）

Fig. 10-2. Mass spectra of diphenylamine
(Upper figure is based on a packed column, lower on a capillary column)

[15]

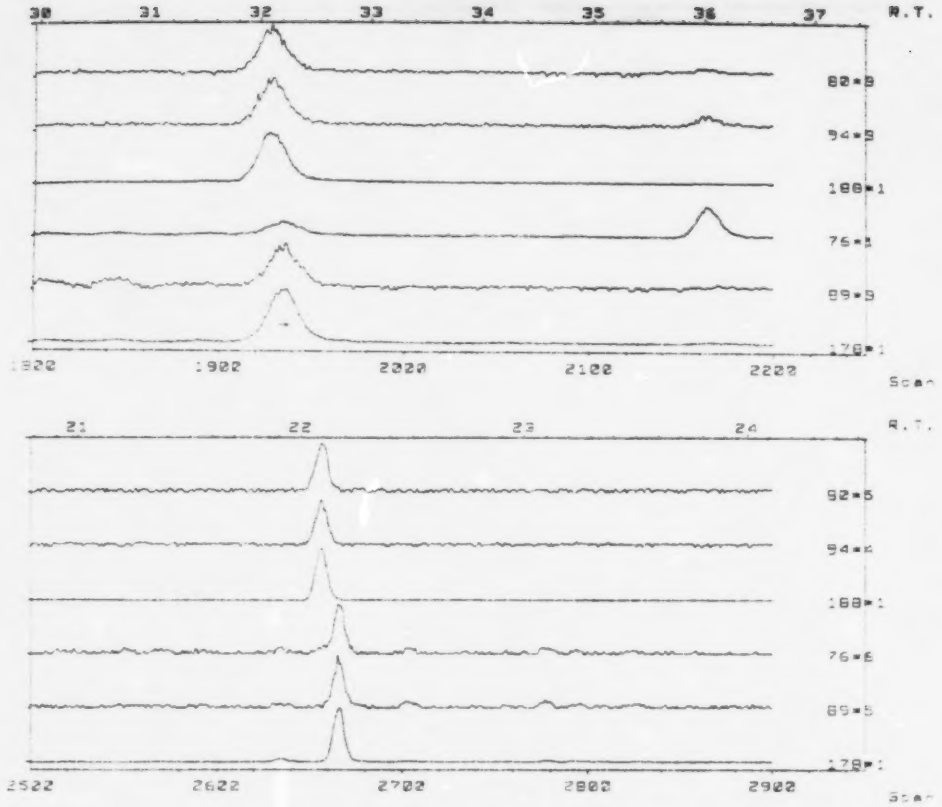

図11-1 アントラセン (m/z 178, 89, 76) と内標準 d_{10}-アントラセン (m/z 188, 94, 80) のマスクロマトグラム (上はパックドカラム, 下はキャピラリーカラムによるもの)

Fig. 11-1. Mass chromatograms of anthrathene (m/z 178, 89, 76) and internal standard d_{10}-anthrathene (m/z 188, 94, 80) (Upper figure is based on a packed column, lower on a capillary column)

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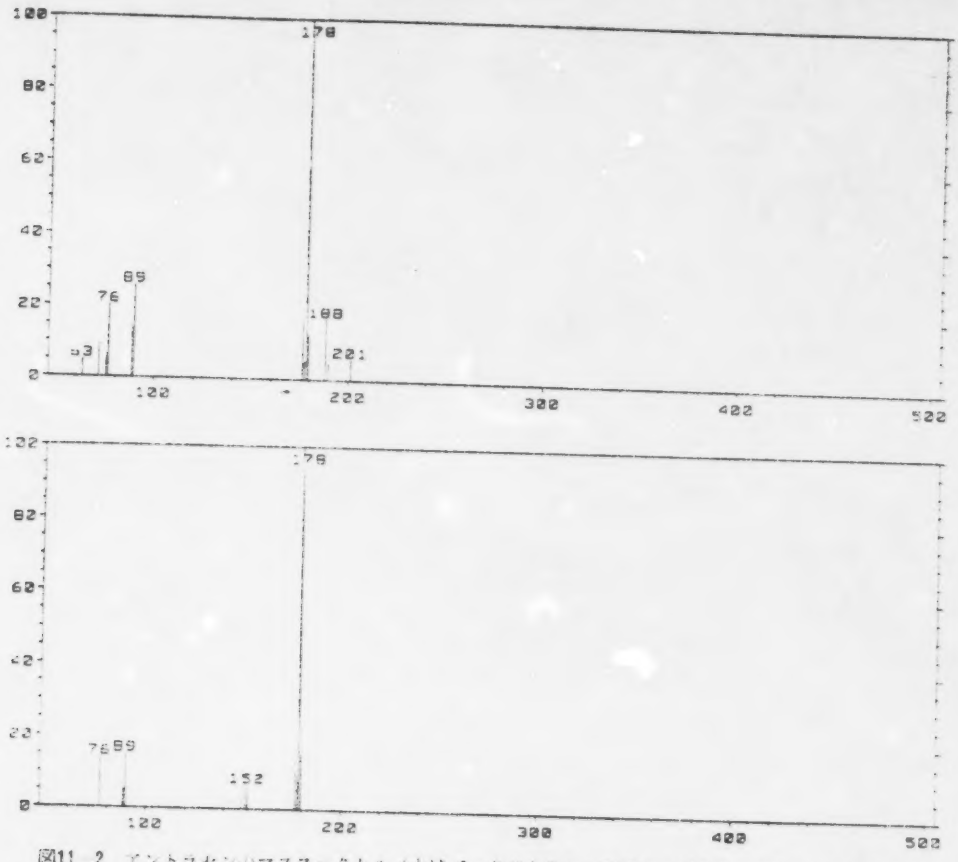

図11-2 アントラセンのマススペクトル（上はパックドカラム，下はキャピラリーカラムによるもの）

Fig. 11-2. Mass spectra of anthrathene (Upper figure is based on a packed column, lower on a capillary column)

[17]

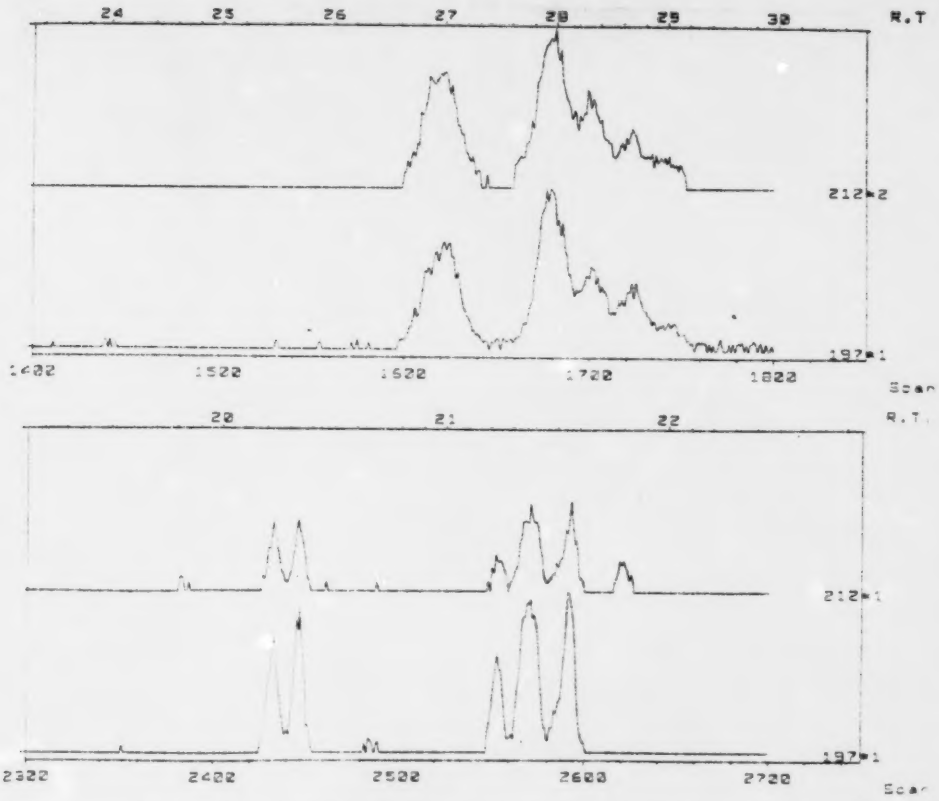

図12—1 ジイソプロピルナフタレン（m/z 197, 212）のマスクロマトグラム
（上はパックドカラム，下はキャピラリーカラムによるもの）

Fig. 12-1. Mass chromatograms of diisopropryl naphthalene (m/z 197, 212) (Upper figure is based on a packed column, lower on a capillary column)

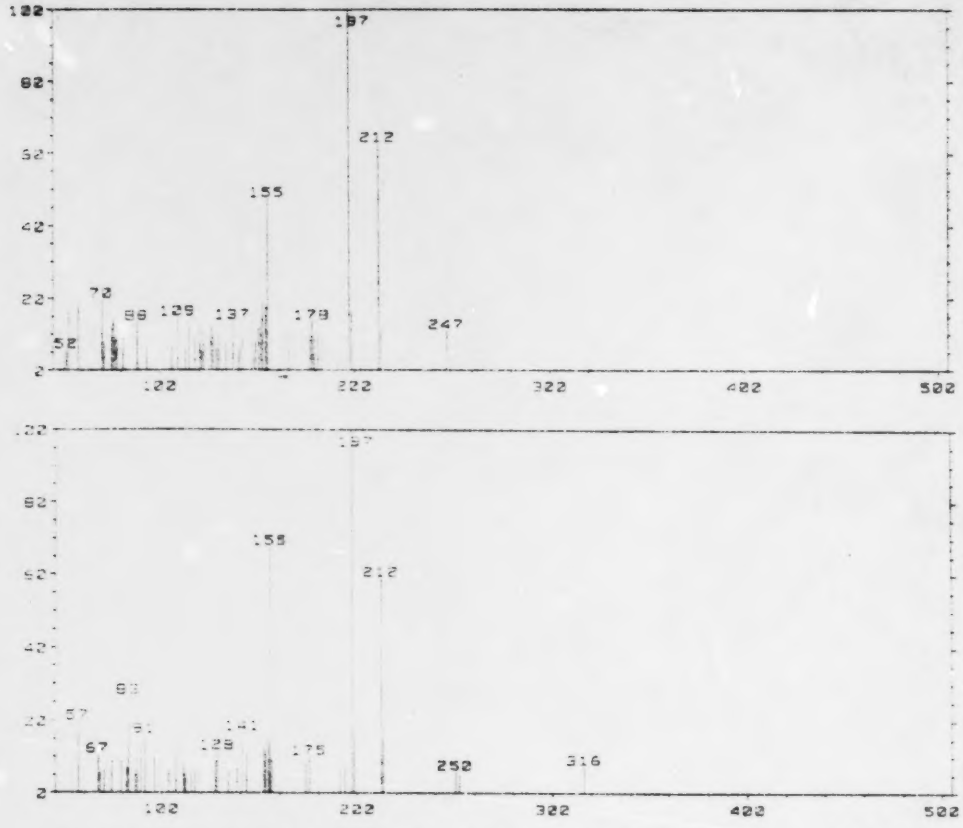

図12-2 ジイソプロピルナフタレンのマススペクトル（上はパックドカラム，下はキャピラリーカラム）

Fig. 12-1. Mass spectra of diisopropyl naphthalene (Upper figure is based on a packed column, lower on a capillary column)

[19]

Table 5. Search results Water sample + standard substances (CAP)

表5 検索結果 水質+標準 (CAP)

	[a] 物質名	[b] S.I. 値	[c] K値	K%	C%	[d] 順位 S.I.	K	K%
1	o-クロロトルエン [e]	—	—	—	—	—	—	—
2	p-ジクロロベンゼン	0.70	79	65	30	1	1	1
3	o-ジクロロベンゼン	0.78	71	58	34	1	2	2
4	2,4-ジクロロトルエン	—	—	—	—	—	—	—
5	1,2,4-トリクロロベンゼン	0.81	90	68	4	1	3	2
6	m-ジブロモベンゼン	0.75	102	73	3	1	3	2
7	m ニトロトルエン	0.82	47	41	18	1	2	3
8	p-ジイソプロピルベンゼン	0.67	51	45	32	1	4	4
9	2,3 キシリジン	—	—	—	—	—	—	—
10	p-クロロフェノール	0.76	x	x	x	1	x	x
11	p-クロロニトロベンゼン	0.77	68	53	27	1	2	1
12	o-クロロ-2-メチルアニリン	—	—	—	—	—	—	—
13	α-メチルナフタレン	0.93	62	54	6	1	2	3
14	2,4-ジクロロアニリン	—	—	—	—	—	—	—
15	2,4-ジクロロニトロベンゼン	0.80	130	83	6	1	1	1
16	2,4,5-トリクロロフェノール	0.72	95	75	5	1	4	3
17	1,2,3,4-テトラクロロベンゼン	0.82	75	54	9	1	2	3
18	p-ニトロアニソール	0.77	x	x	x	1	x	x
19	ビフェニール	0.84	77	68	3	1	2	2
20	ジフェニルエーテル	0.83	90	72	0	1	1	1
21	m-ジニトロベンゼン	0.74	104	71	8	1	1	1
22	リタル酸メチル	0.87	72	65	9	1	1	1
23	α-ナフチルアミン	—	—	—	—	—	—	—
24	ペンタクロロベンゼン	0.79	125	83	0	1	1	1
25	3,4-ジニトロトルエン	0.36	111	69	16	3	1	1
26	4-クロロ-2-ニトロアニリン	0.77	111	77	6	1	1	1
27	1-ニトロナフタレン	0.84	92	72	10	1	1	1
28	リタル酸ジエチル	0.86	79	71	0	1	1	1
29	1-ブロモ-4-フェノキシベンゼン	0.84	86	69	16	1	9	7
30	ジフェニルアミン	0.85	62	54	7	1	3	2
31	p-tert-オクチルフェノール	0.82	48	53	8	1	2	1
32	リン酸トリエチル	0.81	x	x	x	1	x	x
33	ジイソプロピルナフタレン	0.45	x	x	x	2	x	x
34	γ BHC	0.63	157	67	11	2	1	1
35	ペンタクロロニトロベンゼン	0.59	x	x	x	1	x	x
36	イソホロン	0.88	81	72	4	1	3	3
37	ジエチルフタレート	0.66	102	74	20	1	1	1
38	トリエチルホスフェート	0.59	x	x	x	1	x	x
39	リタル酸ブチル	0.82	55	57	0	1	1	1
40	p-ターフェニル	0.93	77	68	12	1	3	1
41	リン酸トリフェニル	0.76	117	75	11	1	1	1

[a] Substance name
[b] S.I. value
[c] K value
[d] Ranked S.I.
[e] [Substances listed identically to Table 3]

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Table 6. Search results Water sample + standard substances (PAC)

表6 検索結果 水質+標準 (PAC)

	[a] 物質名	[b] S.I.値	[c] K値	K%	C%	[d] 順位 S.I.	K	K%
1	o-クロロトルエン [e]	0.79	78	64	31	1	1	5
2	p-ジクロロベンゼン	0.83	100	82	0	1	1	1
3	o-ジクロロベンゼン	0.86	99	80	15	1	2	3
4	2,4-ジクロロトルエン	0.62	93	76	13	1	3	3
5	1,2,4-トリクロロベンゼン	0.86	110	83	12	1	3	3
6	m-ジブロモベンゼン	0.35	90	70	50	9	3	1
7	m-ニトロトルエン	0.84	81	70	2	1	1	2
8	p-ジイソプロピルベンゼン	0.72	75	65	14	1	11	7
9	2,3-キシリジン	—	—	—	—	—	—	—
10	p-クロロフェノール	—	—	—	—	—	—	—
11	p-クロロニトロベンゼン	0.64	x	x	x	1	x	x
12	o-クロロ-2-メチルアニリン	—	—	—	—	—	—	—
13	α-メチルナフタレン	0.95	76	67	5	1	2	2
14	2,4-ジクロロアニリン	—	—	—	—	—	—	—
15	2,4-ジクロロニトロベンゼン	0.41	x	x	x	3	x	x
16	2,4,5-トリクロロフェノール	—	—	—	—	—	—	—
17	1,2,3,4-テトラクロロベンゼン	0.88	115	83	8	1	2	3
18	p-ニトロアニソール	0.68	x	x	x	1	x	x
19	ビフェニール	0.87	102	89	0	1	1	1
20	ジフェニルエーテル	0.82	89	71	19	1	1	1
21	m-ジニトロベンゼン	—	—	—	—	—	—	—
22	フタル酸ジ-n-ブチル	0.90	85	77	6	1	1	1
23	α-ナフチルアミン	—	—	—	—	—	—	—
24	ペンタクロロベンゼン	0.78	125	83	16	1	1	1
25	3,4-ジニトロトルエン	—	—	—	—	—	—	—
26	4-クロロ-2-ニトロアニリン	0.61	x	x	x	1	x	x
27	1-ニトロナフタレン	0.56	x	x	x	1	x	x
28	フタル酸ジエチル	0.85	79	91	0	1	1	1
29	4,4'-ジメチルビフェニール	0.78	79	63	16	1	9	7
30	ジフェニルアミン	0.82	68	55	43	1	7	8
31	p-tert-オクチルフェノール	0.75	39	43	42	1	1	1
32	リン酸トリブチル	0.80	49	45	20	1	1	1
33	ジイソプロピルナフタレン	0.66	x	x	x	1	x	x
34	γ-BHC	0.58	106	63	43	2	4	3
35	ペンタクロロニトロベンゼン	—	—	—	—	—	—	—
36	アントラセン	0.87	63	56	29	1	5	5
37	ジエチルビフェニール	0.80	132	87	34	1	1	1
38	トリエチルビフェニール	0.56	x	x	x	1	x	x
39	フタル酸ジブチル	0.80	44	45	0	1	1	1
40	p-ターフェニル	0.87	88	64	17	1	1	2
41	リン酸トリフェニル	0.79	97	63	8	1	1	1

[a] Substance name
[b] S.I. value
[c] K value
[d] Ranked S.I.
[e] [Substances listed identically to Table 3]

Table 7. Search results Sediment sample + std. substances; neutral fraction-1 (CAP)
Sediment sample + std. substances; neutral fraction-2 (CAP)

表7 検索結果 底質＋標準，中性分画—1 (CAP)
底質＋標準，中性分画—2 (CAP)

[21]

	[a] 物質名	[b] S.I. 値	[c] K値	K%	C%	[d] 順位 S.I.	K	K%
1	o-クロロトルエン	—	—	—	—	—	—	—
2	p-ジクロロベンゼン [e]	0.78	64	52	34	1	1	2
3	o-ジクロロベンゼン	0.74	x	x	x	1	x	x
4	2,4-ジクロロトルエン	0.37	x	x	x	1	x	x
5	1,2,4-トリクロロベンゼン	0.74	75	56	39	1	2	3
6	m-ジブロモベンゼン	0.66	82	57	41	1	1	1
7	m-ニトロトルエン	0.79	81	70	31	1	1	1
8	p-ジイソプロピルベンゼン	0.55	51	41	44	2	4	4
9	2,3-キシリジン	—	—	—	—	—	—	—
10	p-クロロフェノール	—	—	—	—	—	—	—
11	p-クロロニトロベンゼン	0.55	x	x	x	1	x	x
12	o-クロロ-2-メチルアニリン	—	—	—	—	—	—	—
13	α-メチルナフタレン	0.85	82	72	31	1	1	1
14	2,4-ジクロロアニリン	0.71	67	50	41	1	2	4
15	2,4-ジクロロニトロベンゼン	0.62	87	52	28	1	1	1
16	2,4,5-トリクロロフェノール	—	—	—	—	—	—	—
17	1,2,3,4-テトラクロロベンゼン	0.76	74	54	32	1	2	2
18	p-ニトロアニソール	0.68	83	65	27	1	1	1
19	ビフェニール	0.80	71	62	3	1	2	2
20	ジフェニルエーテル	0.84	90	72	1	1	1	1
21	m-ジニトロベンゼン	0.51	x	x	x	2	x	x
22	フタル酸ジメチル	0.74	63	57	47	1	2	1
23	α-ナフチルアミン	—	—	—	—	—	—	—
24	ペンタクロロベンゼン	0.59	82	55	50	1	1	1
25	3,4-ジニトロトルエン	—	—	—	—	—	—	—
26	4-クロロ-2-ニトロアニリン	—	—	—	—	—	—	—
27	1-ニトロナフタレン	0.73	88	69	38	2	1	1
28	フタル酸ジエチル	0.50	x	x	x	1	x	x
29	4,4'-ジメチルビフェニール	0.85	92	74	14	1	3	1
30	ジフェニルアミン	0.75	77	67	9	1	1	1
31	p-tert-ブチルフェノール	0.80	37	41	13	1	9	4
32	[illegible]	0.72	x	x	x	1	x	x
33	ジイソプロピルナフタレン	0.55	x	x	x	1	x	x
34	γ-BHC	0.49	133	56	37	2	1	1
35	ペンタクロロニトロベンゼン	—	—	—	—	—	—	—
36	アントラセン	0.82	75	66	7	2	4	3
37	ジエチルビフェニール	0.70	74	56	32	1	6	7
38	トリエチルビフェニール	0.40	x	x	x	1	x	x
39	フタル酸ジブチル	0.78	42	44	29	1	1	1
40	p-メーフェニト	0.89	61	52	11	1	4	3
41	リン酸トリフェニル	—	—	—	—	—	—	—

[a] Substance name
[b] S.I. value
[c] K value
[d] Ranked S.I.
[e] [Substances listed identically to Table 3]

4. Search results [22]

Collecting the mass spectra in respect of the 41 substances added to the water samples and sediment samples, searches were carried out using 1) the PTRI-fed mass spectral search system developed on this occasion, and 2) the mass spectral search system based on the erstwhile PBM method.

The index of mass spectral evaluation for the PTRI-fed search is SI, but unlike the erstwhile SI method, it is only after the search target has been narrowed down by PTRI that the SI is determined, so that a search in order of high ranking is its distinctive characteristic. The ranking is an important element of search efficiency.

The PBM method evaluates the mass spectra by the K value and K% which express the degree of match of peaks high in specificity and C% which expresses the proportion of impure peaks. The search target encompasses all substances in the EPA/NIH/MSDB mass spectral data base. They are ranked in order of high K value and K%.

Table 5 shows the mass spectral search results when the standard substances were added to water samples and analyzed with a capillary column. As well, Table 6 shows the search results in the case where the same samples were analyzed with a packed column, while Table 7 shows the case where the standard substances were added to sediment samples and analyzed with a capillary column.

In the tables, - denotes the case where mass spectra could not be collected, while X denotes the case where no retrieval was made under the established conditions for a PBM search (K value 20 or over, K% 30 or over, C% 50 or under and ranking within 10).

If we compare the quality of the mass spectra of the aforesaid packed column and capillary column, with diphenylamine and anthrathene the SI is higher and the C% is lower with the capillary column. The reason why there is not much difference in SI is because a reverse search method to evaluate the degree of

matching of the reference data from the sample data has been applied. The proportion of the mixed peaks seen in Fig. 10-2 and Fig. 11-2 revealed a marked difference in C%. Even in K value and K% ranking, the data based on a capillary column score high. In the case of diisopropylnaphthalene, more isomers are intermixed in the packed column and the peak strength became stronger, whereby the SI is thought to have become high.

With substances of low boiling point (those with a low substance number in the table), there being the problem of the injection method among other things, the SI is lower in the capillary data. However, as with m-dibromobenzene, where in the packed case there is an overlap with the internal standard naphthalene-d_8 and separation cannot be achieved, the effectiveness of the capillary column is great.

At high boiling point the background of the environmental samples rises, and the separability impacts greatly on search efficiency. Also, in the sediment samples the chemical substances contained are numerous, and as can be seen in the TIC of Figs. 8-6 and 8-7 as well as Table 7, even though the selfsame capillary column is used, the quality of the search results is quite low compared to the water samples. In such cases, were we dealing with mass spectra analyzed and collected with a packed column, the search results would be thought to be poorer still.

Next we examined the search efficiency of the PTRI-fed mass spectral search system and the PBM search system. The index of mass spectral evaluation for PTRI search is SI, and this was calculated and determined in every case where spectral retrieval was possible. In the analysis by capillary column among the substances added to the water samples, those whose SI turned out to be under 0.5 were 3,4-dinitrotoluene and diisopropyl naphthalene. The reason for the low SI in the case of 3,4-dinitrotoluene is thought to be because the peak was so low in strength that spectral retrieval was not possible with a packed column, while

diisopropyl naphthalene being one of the isomers the peak was low in strength. The rest were 0.5 or above in SI and generally satisfactory. As the search target had been narrowed down by establishing the limits of PTRI, in terms of ranking virtually all ranked 1 and at worst no more than 3.

When a search was made by the PBM method with the same data, triethyl biphenyl not being stored in the reference data naturally could not be retrieved. p-chlorophenol, p-nitroanisole, tributyl phosphate and diisopropyl naphthalene did not meet the search parameters so were not retrieved. Furthermore, the K value and K% ranking did not necessarily turn out to be 1 as well. This is thought to be attributable to a problem with the quality of the mass spectra being stored and the fact that the search target encompasses all substances.

With the data on the sediment samples, the substances which could not be correctly retrieved by the PBM search increased even more, but in the PTRI search the SI ranking of those with low SI value still became 1 or 2.

Comparing the retrieval time, it turned out to be 10-15 seconds per substance in the sample data in the PTRI search and 7-8 minutes per substance in the PBM search. Hereafter if the number of stored substances with PTRI-fed data increases, the retrieval time can be thought to increase somewhat as well, but because it is not as though all the substances become the target of search like in the PBM search, this search system can be said to be short in retrieval time and good in efficiency. Another thing is that it can be amply handled by a personal computer which is inferior in processing capability to a large-scale general purpose computer.

In cases where the SI ranking was not 1, errors could be prevented by checking the matching of the structural characteristic ions output at the same time. Also by spectral comparison using graphics, the spectra in the respective ranking can be easily confirmed, making the probability of error extremely low.

In this way, for chemical substance searches in environmental samples, the PTRI-fed mass spectral search method was found to be extremely effective.

Summary [23]

In the search and identification in GC/MS analysis of chemical substances in the environment, because of the fact that the samples are multi-component mixtures there are many cases where only insufficiently separable mass spectra can be obtained, and with the existing search systems there had been many problem points such as failing to retrieve the target substance. Accordingly, by improving the means of separation of chemical substances or mass spectra and utilizing GC separation data in the search, a GC/MS data analysis system suited to environmental analysis was developed.

The PTRI and structural characteristic ions which are the GC separation data were stored in the data base together with the mass spectra. In the search the PTRI was used as a pre-search parameter, while SI was used in the mass spectral evaluation to do the search.

In that the PTRI is data different in nature from the mass spectra, substances similar in mass spectra can be distinguished, and the accuracy of identification improved a good notch.

Adding 41 substances to environmental samples, an examination was made as to whether or not the target substances would be properly retrieved. In the case where a packed column was used for the GC column, mixed peaks emerged due to insufficient GC separation and instances could be seen where mass spectral retrieval was difficult, but when a capillary column was used wholesale improvements occurred.

Compared to searches by the erstwhile PBM method, the retrieval rankings rose and the retrieval time was shortened substantially.

In order to carry out searches of even higher reliability, there is a need for measures to improve the separability of mixed components such as by utilizing a capillary column as well as for control of accuracy of the apparatus. Hereafter, we should like to increase the number of stored substances in the data base and aim for practical applications such as searches for unknown substances.